Effect of Fluorocarbon and Hydrocarbon Chain Lengths In Hybrid Surfactants for Supercritical CO_2

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Abstract

Hybrid surfactants containing both fluorocarbon (FC) and hydrocarbon (HC) chains have recently been shown to solubilize water and form elongated reversed micelles in supercritical CO_2. To clarify the most effective fluorocarbon (FC) and hydrocarbon (HC) chain lengths, the aggregation behavior and interfacial properties of hybrid surfactants FC*m*-HC*n* (FC length *m* / HC length *n* = 4/2, 4/4, 6/2, 6/4, 6/5, 6/6 and 6/8) were examined in W/CO_2 mixtures as functions of pressure, temperature, and water-to-surfactant molar ratio (W_0). The solubilizing power of hybrid surfactants for W/CO_2 microemulsions was strongly affected by, not only the FC length, but also that of the HC. Although the surfactants having short FC and/or HC tails (namely, *m*/*n* = 4/2, 4/4, and 6/2) did not dissolve in supercritical CO_2 (even at ~17 mM, ≤ 400 bar, temperature ≤ 75 ºC, and W_0 = 0-40), the other hybrid surfactants were able to yield transparent single-phase W/CO_2 mixtures identified as microemulsions. The solubilizing power of FC6-HC*m* surfactants reached a maximum (W_0 ~80 at 45 ºC and 350 bar) with a hydrocarbon length, *m*, of 4. The W_0 value of 80 is the highest for a HC-FC hybrid surfactant, matching the highest value reported for a FC surfactant which contained more FC groups. High-pressure SANS measurements from FC*m*-HC*n*/D_2O/CO_2 microemulsions were consistent with growth of the microemulsion droplets with increasing W_0. In addition, not only spherical reversed micelles but also non-spherical assemblies (rod-like or ellipsoidal) were found for the systems with FC6-HC*n* (*n* = 4-6). At fixed surfactant concentration and W_0 (17mM and W_0 = 20). The longest reversed micelles were obtained for FC6-HC6 where a mean aspect ratio of 6.3 was calculated for the aqueous cores.

Keywords: Supercritical CO_2, Microemulsion, Hybrid surfactant, Solubilizing power, Small-Angle Neutron Scattering

1. Introduction

Supercritical CO_2 ($scCO_2$) has received much attention for use in industrial applications due to attractive properties such as low cost, inflammability, environmentally benignity, natural abundance, high mass transfer, and pressure/temperature-tunable solvency (or CO_2 density) [1]. $ScCO_2$ is currently used as a green solvent for organic synthesis, dry cleaning, polymerization, extraction, nanomaterial processing amongst others. Unfortunately, supercritical CO_2 can dissolve only nonpolar and small molecular mass materials, with large polar materials always separating in neat $scCO_2$[2]. Improving the poor solubility of polar materials is important for developing the potential applications of $scCO_2$. One of the most promising approaches to increase the solubility of polar substances is to form reversed micelles with high-polarity aqueous cores in the continuous $scCO_2$ phase, that is, water-in-$scCO_2$ microemulsions (W/CO_2 μEs).[2] Since such organized fluids have the attractive characteristics of $scCO_2$, as well as the solvation properties of bulk water, they have potential as volatile organic compound (VOC)-free and energy-efficient solvents for nano-material synthesis, enzymatic reactions, dry-cleaning, dyeing, and preparation of inorganic/organic hybrid materials[2].

To be a viable green and economical technology, the amount of surfactant used for W/CO_2 μEs should be as small as possible, and this needs to be balanced against the need for large interfacial areas in W/CO_2 μEs and appropriate levels of dispersed water needed to enhance process efficiencies. One approach to meet these requirements is to explore or develop highly efficient solubilizers for W/CO_2 μEs, and studies aiming to do this started in the 1990s.[3]

The development of CO_2-philic hydrocarbon surfactants for $scCO_2$ has been recognized as an important task for economic and environmental reasons.[3-6] However, most commercial and known hydrocarbon surfactants are insoluble and inactive in $scCO_2$ systems[3]. Note that the commercial analogue Aerosol-OT (sodium bis-(2-ethyl-1-hexyl) sulfosuccinate, AOT) is insoluble in $scCO_2$ and hence ineffective at stabilizing W/CO_2 μEs.[3] In this regard, it became apparent that conventional surfactant-design theory cannot be applied to W/CO_2 systems, and that CO_2-philicity is not directly comparable to oleo-philicity. Therefore, advancing molecular-design theory for CO_2-philic surfactants has required new

directions and paradigms in the field of surfactants. In current studies for CO_2-soluble compounds, highly branched hydrocarbons[4,5], especially methyl-branches, ester and ether groups have been reported to increase solubility in $scCO_2$. Unfortunately, an efficient and cost effective hydrocarbon stabilizer for W/CO_2 μEs, like the AOT used commonly for W/O μEs[6], has not yet been found.

Many earlier studies reported that several fluorinated surfactants, including perfluoropolyether (PFPF) surfactants and fluorinated AOT analogues, could dissolve in CO_2 and exhibit a high interfacial activity at the W/CO_2 interface, suggesting the feasibility of forming W/CO_2 μEs.[7-10] The water-solubilizing power in CO_2 was often discussed in terms of the water-to-surfactant molar ratio W_0 (=[water]/[surfactant]). Hereafter, the maximal W_0 achievable in a single-phase W/CO_2 microemulsion, namely W_0^{max}, is used to evaluate the solubilizing power. In the cases of PFPE surfactants the reported W_0^{max} reached ~20.[7-10]

It is not understood why such fluorocarbon surfactants are so good for solubilization of water in $scCO_2$. Recent molecular simulation studies[11,12] have elucidated that when compared with HC chains, FC groups have (1), stronger interactions with CO_2 via quadrupolar and dispersion interactions, and (2), weaker FC-FC chain-chain interactions which are due to a weak repulsion, electrostatic in origin. These properties conspire together to give FC surfactant reversed micelles with better solvation by CO_2, and this causes lower surfactant interfacial packing densities, and weaker attractive inter-micellar interactions compared with hydrocarbon surfactant analogues.

Recently, with the aim of optimizing the surfactant structure of fluorinated AOT analogues for W/CO_2 μEs, double-FC-tail anionic surfactants with various FC lengths[13] and sulfoglutarate/sulfosuccinate headgroups were examined to probe the effect of not only FC length, but also the addition of methylene spacers between double tails. This examination found that the solubilizing powers of the glutarates nFG$(EO)_2$ were higher than those of the succinate analogues nFS$(EO)_2$, and the most efficient surfactant was found to be 4FG$(EO)_2$ at 75°C (W_0^{max} = 80) despite having the shortest FC (perfluorobutyl) tails.[13] Considering that fluorocarbons are CO_2-philic groups and longer FC surfactants generally have higher solubilising power,[3,7-12] the fact that this can be obtained by the shortest FC

$4FG(EO)_2$ is at first sight surprising. In further studies, the minimum fluorine content necessary to render a surfactant CO_2-philic has been identified by using double-pentyl-tail surfactants with different fluorination levels[14]. In these surfactants, at least two fluorinated carbons (CF_3CF_2-) were required to stabilize W/CO_2 μEs.[14] Through the studies mentioned above, the understanding behind the effect of FC-tail length on the solubilizing power for symmetrical double FC-tail surfactants (i.e. fluorinated AOT-analogues) has been becoming clearer year-by-year.

As with the fully fluorinated surfactant series, two-tail hybrid surfactants, having separate HC and FC chains in the same molecule, have also been evaluated for stabilization of W/CO_2 microemulsions. The first successful example of a CO_2-philic hybrid surfactant was sodium 1-pentadecafluoroheptyl-1-octanesulfate (F7H7, $(C_7H_{15})(C_7F_{15})CHOSO_3Na$), which solubilized water up to $W_0^{max} = 35$.[15] Further studies[16] of hybrid surfactants related to F7H7 but with different FC and HC chain lengths, observed the formation of W/CO_2 μEs for most of the analogues, but smaller attainable W_0^{max} values than for F7H7. On the other hand, these hybrid surfactant systems were often reported to form elongated reversed micelles[16], whereas those formed by non-hybrid surfactants are likely to be spherical. The formation of elongated aggregates with a high aspect ratio (rod length/diameter) can thicken dense CO_2 and will be a viable way to achieve higher efficiencies in enhanced oil recovery[17]. Unfortunately, these unique characteristics have never been examined in detail in terms of the hybrid tail structure (e.g. effect of FC and HC length and the balance of both).

How does a hybrid surfactant stabilize the W/CO_2 microemulsion to form elongated reversed micelles? What is the role of the non-CO_2-philic HC-tail? These questions have never been clarified yet could be very interesting and important topics for chemists in this field. To advance CO_2-philic surfactant design theory, this study has focused on the effect of the hybrid tail structure (e.g. FC-HC balance) on solubilizing power, aggregate size and shape in $scCO_2$. This provides important information on the structure-property correlations of hybrid surfactants such as hydrophilic/CO_2-philic balance (HCB)[18], critical packing parameter (CPP)[19], interactions between tail-tail and tail-head groups[20].

Recently, a series of the hybrid surfactant, sodium 1-oxo-1-[4-(perfluoroalkyl)phenyl]alkane-2-sulfonates, FC*m*-HC*n* (FC length *m* = 6, HC length *n* = 2, 4, 6 and 8) were examined for formation of W/CO_2 systems.[21] However, insufficient data were available to clarify the effect of the FC and HC lengths of the hybrid surfactant on phase stability, and also on the nanostructures of reversed micelles. To reveal the separate roles of FC and HC tails, this study examined in detail the phase behavior, solubilizing power, and aggregate nanostructure for seven FC*m*-HC*n* compounds (*m*/*n* = 4/2, 4/4, 6/2, 6/4, 6/5, 6/6, and 6/8) in scCO_2 by using high-pressure UV-vis light absorbance and small-angle neutron scattering (SANS). The significance of this study to the field of surfactant science is that optimized, super-efficient, low fluorine containing surfactants are now available for stabilization of W/CO_2 μEs and formation of CO_2-philic elongated reversed micelles.

2. Experimental Section

2.1. Materials

The family of surfactants were based on the hybrid surfactant sodium 1-oxo-1-[4-(perfluoroalkyl)phenyl]alkane-2-sulfonates, FC*m*-HC*n* (FC length *m* = 4 or 6, HC length *n* = 2, 4, 5, 6 and 8) and the non-hybrid analogue surfactant sodium 1-oxo-1-[4-(hexyl)phenyl]-2-hexanesulfonates, HC6-HC6. The surfactants FC*m*-HC*n* with *m*/*n* = 4/2, 4/4, 6/2, 6/6, and 6/8 and HC6-HC6 were provided by Prof. Yoshino and Dr. Kondo at Tokyo University of Science. The other surfactants FC6-HC4 and FC6-HC5 were synthesized and purified as described in supporting information. For the synthesis, iodo-benzene, hexanoyl chloride, heptanoyl chloride were purchased from Tokyo Chemical Industries, and used without further purification. Reagent grade 1,4-dioxane, 1,2-dichloroethane, copper powder, sodium hydroxide were commercially obtained from Wako Pure Chemical Industries and employed as received. Tridecafluorohexyl iodide and sulphur trioxide were purchased from Synquest laboratories and Nacalai tesque, respectively.

Structures of FC*m*-HC*n*, HC6-HC6, and the other control hybrid surfactants F*m*H*n* are shown in **Table 1** along with the interfacial properties of aqueous solutions obtained by standard measurements[22,23]. Ultrapure water with a resistivity of 18.2 MΩ cm was generated from a Millipore Milli-Q Plus system. CO_2 was of 99.99% purity (Ekika Carbon Dioxide Co., Ltd.). The structures of the steric models and the length of one surfactant molecule in the absence of other molecules were calculated by MM2 (Molecular Mechanics program 2) calculations (Chem 3D; CambridgeSoft Corp., Cambridge, MA).

2.2. Surface tension measurements

Surface tensions of aqueous surfactant solutions were measured using a Wilhelmy tensiometer (CBVP-Z, Kyowa Interface Science) equipped with a platinum plate. The measurements were performed at 35 ± 0.1 °C until constant values of the surface tension of the aqueous surfactant solutions were obtained; the experimental error was less than 0.1 mN/m. The critical micelle concentration (CMC) was

obtained from the point of intersection of the curves in the graph of surface tension versus logarithm of the surfactant concentration.

2.3. Phase behavior and UV-visible absorption spectral measurements

A high-pressure vessel with an optical window and a moveable piston inside the vessel was used to observe phase behaviour of surfactant/water/scCO_2 mixtures with varying pressure and temperature. A detailed description of the experimental apparatus and procedures for the measurements can be found elsewhere.[13,14]

In order to examine formation of aqueous cores in W/CO_2 μEs, UV-visible absorption spectroscopy measurements were performed using methyl orange (MO) as a trace marker dye, on a double-beam spectrophotometer (Hitachi High-Technologies, Co., U-2810), with a quartz window pressure cell (volume: 1.5 cm^3) that was connected to the experimental apparatus. The cell was made of stainless steel (SUS316) and had three quartz windows with a thickness of 8 mm. Each window had an inner diameter of 10 mm and was positioned so as to provide a perpendicular 10-mm optical path. Each window was attached to the stainless steel body of the cell using PTFE kel-F packing. The windows were fastened tightly to the steel body, thereby compressing the packing between the stainless steel parts and the quartz window and providing excellent sealing (tested up to 400 bar). The temperature of the cell was controlled by circulating water with a thermostat bath. Spectroscopic measurements were performed and the resulting absorption spectra of the cell windows were compared with those of a standard quartz cell for an aqueous MO solution at ambient pressure; it was observed that both the spectra were in good agreement with each other.

The measurements of the water/surfactant/scCO_2 systems were performed at temperatures of 35 – 75 °C and pressures of lower than 400 bar. The densities of CO_2 were calculated using the Span-Wagner equation of state (EOS)[34]. Pre-determined amounts of surfactant and CO_2 (20.0g), where the molar ratio

of surfactant to CO_2 was fixed at 8×10^{-4}, were loaded into a variable-volume high-pressure optical cell. Then, water or an aqueous MO solution (3 mmol L^{-1}), was added into the optical cell through a six-port valve until the clear Winsor-IV W/CO_2 μE (i.e. single-phase W/CO_2 μE) solution became a turbid macroemulsion or a precipitated hydrated surfactant. Surfactant molar concentration was in the range 10-20 mmol L^{-1}, for example 16.7 mmol L^{-1} at 45 ºC and 350 bar, as the inner volume of the cell was varied by changing experimental pressure and temperature.

During spectroscopic measurements, the scCO_2 mixture was stirred and circulated between the optical vessel and the quartz window cell until a constant absorbance was attained. The circulation was then discontinued; the valves between the vessel and the quartz window cell were closed, and the measurement was performed. The physical properties of the continuous phase of scCO_2 were assumed to be equivalent to those of pure CO_2.

2.4 High-Pressure Small-Angle Neutron Scattering (HP-SANS) measurements and data analysis

Due to the range of neutron wavelengths available, time-of-flight SANS is suitable for studying the shapes and sizes of colloidal systems. High-pressure SANS (HP-SANS) is a particularly important technique for determining surfactant aggregation structure in supercritical CO_2. The HP-SANS measurements of the D_2O/surfactant/scCO_2 systems were performed at 45 °C and 350 bar. The LOQ time-of-flight instrument, at the Rutherford Appleton Laboratory at ISIS UK, was used in conjunction with a stirred high-pressure cell (Thar). The path length was 10 mm, the neutron beam diameter was 10 mm. The measurements gave the absolute scattering cross section $I(Q)$ (cm^{-1}) as a function of momentum transfer Q ($Å^{-1}$), which is defined as $Q = (4\pi/\lambda)\sin\theta$, where θ is the scattering angle. The accessible Q range was 0.007-0.22 $Å^{-1}$, arising from an incident neutron wavelength λof 2.2-10 Å. The data were normalized for transmission, empty cell, solvent background, and pressure induced changes in cell volume as before.[13]

Pre-determined amounts of D_2O and surfactant, where the molar ratio of surfactant to CO_2 was fixed at 8×10^{-4} (= 10-20 mM at the appropriate experimental condition), were loaded into the Thar cell.

Then, CO_2 (11.3g), was introduced into the cell by using a high pressure pump, and the surfactant/D_2O/CO_2 mixture was pressurized up to 350 bar at 45 ºC by decreasing the inner volume of the Thar cell. With vigorous stirring, visual observation was carried out to identify the mixture as being a transparent single-phase W/CO_2 µE or other turbid phase. Finally, the HP-SANS experiment was performed for not only the single-phase W/CO_2µE, but also the turbid phase below a cloud point phase transition pressure P_{trans}. Because these are dilute solutions/dispersions, the physical properties of the continuous phase of scCO_2 were assumed to be equivalent to those of pure CO_2.

Neutrons are scattered by short-range interactions with sample nuclei, with the "scattering power" of different components being defined by a scattering-length density (SLD), ρ (cm^{-2}). For CO_2, ρ_{CO2} ~ 2.50 × mass density × 10^{10} cm^{-2} [25]; at the experimental pressure of 350 bar and temperature of 45 ºC, the CO_2 density is 0.917 g cm^{-3} so that ρ_{CO2}~ 2.29 × 10^{10} cm^{-2}. The scattering length density of surfactant (ρ_{surf}) and D_2O (ρ_{D2O}) were obtained using;

$$\rho = \sum_i b_i / V_m \qquad (1)$$

b_i is the nuclear scattering lengths as given in the literature[26] and V_m is the molecular volume, which can be obtained from the mass density. Mass densities of FC6-HC*n* (*n* = 4, 5, 6, and 8) were assumed to be 1.3 g/cm^3 as 1.7 g/cm^3 for a typical fluorinated compound[27] and 1.0 g/cm^3 for a hydrocarbon surfactant. The calculated scattering length densities for the FC6-HC*n* (*n* = 4, 5, 6, and 8) were 2.26 × 10^{10} cm^{-2} (*n* = 4), 2.20 × 10^{10} cm^{-2} (*n* = 5), 2.11 × 10^{10} cm^{-2} (*n* = 6) and 2.03× 10^{10} cm^{-2} (*n* = 8), respectively. As the other surfactants FC4-HC*n* (*n* = 2 and 4) and FC6-HC2 and HC6-CH6 did not show any SANS under these conditions, their scattering length densities have been omitted. The scattering length density of D_2O at 45 ºC was calculated to be ~ 6.32 × 10^{10} cm^{-2}. SANS scattering from the D_2O/CO_2 microemulsions with FC6-HC*m* shells was assumed to be from only the so-called water core contrast, because of very similar scattering densities of surfactant and CO_2. Samples in pure CO_2 (11.3 g) were run at the constant molar ratio of surfactant to CO_2 of 8.0 × 10^{-4}.

For model fitting data analysis the W/CO_2 μE droplets were treated as cylindrical and ellipsoidal particles with a Schultz distribution in core radius and length.[28] The polydispersities in rod radius and length were fixed at 0.3 as found in spherical D_2O/CO_2 microemulsions with the double FC-tail surfactants (polydispersity = 0.2-0.4).[29] Full accounts of the scattering laws are given elsewhere[16,23,29-32].

Data have been fit to models as described above using the SasView small-angle scattering analysis software package (http://www.sasview.org/).[32] The fitted parameters are the core radii perpendicular to the rotation axis ($R_{f\text{-}ell,a}$) and along the rotation axis ($R_{f\text{-}ell,b}$) for ellipsoidal particle, or the core radius $R_{f\text{-}cyl}$ and the length $L_{f\text{-}cyl}$ for cylinder particle; these were initially obtained by preliminary Guinier analyses[33] ($L_{g\text{-}cyl}$, $R_{g\text{-}cyl}$, and $R_{g\text{-}sph}$).

3. Results and Discussion

3.1 Interfacial Properties in Water and microemulsion stabilizing ability in $scCO_2$

Table 1 shows basic surfactant properties Krafft temperature, critical micelle concentration (CMC), surface tension at the CMC (γ_{CMC}), and the minimal effective area per molecule (A_{min}). These values except for FC6-HC5 and HC6-HC6 have been reported previously, and are from the literature[22]. Values for FC6-HC5 and HC6-HC6 were obtained through surface tension (γ) measurements and visual observation of the aqueous surfactant solutions. The behaviour of γ as a function of concentration for both surfactants is given in supporting information (Figure SI2). The parameter γ_{CMC} is especially important in predicting the solubilizing power of surfactant in $scCO_2$[13,14,21]; this is because (1) the water/air and water/CO_2 interfacial properties of the surfactant are correlated, and (2) microemulsions generally form at an interfacial tension below 1 mN/m.[34,35]

Interfacial properties of hybrid surfactants, F*m*H*n* (*m*/*n* =7/4, 8/4, 7/7, 8/8) [16,23,17], are listed in Table 1 and were employed as a control hybrid surfactant. In comparison with the F*m*H*n* series (γ_{CMC} = 21.6-25.4 mN m^{-1} and A_{min} = 61-68 $Å^2$), FC4-HC*n* had similar γ_{CMC} (22.5-24.0 mN m^{-1}) but larger A_{min} values (81-89 $Å^2$). Increasing the FC length of FC4-HC*n* to form (FC6-HC*n*), produced lower γ_{CMC} values (16.2-21.5 mN m^{-1}) in spite of the larger A_{min} values (72-105 $Å^2$), indicating less dense intermolecular packing at the surface. The lower γ_{CMC} values of FC*m*-HC*n* with shorter FC tails were presumably attained due to the structural differences, that is, the presence of a benzene ring and/or the head group (sulfonate/sulphate). These low γ_{CMC} values imply increased abilities of FC*m*-HC*n* to lower W/CO_2 interfacial tension and stabilize W/CO_2 microemulsions.[13,14,21] On the other hand, the hydrocarbon surfactant HC6-HC6 (which is the analogue of FC6-HC6) exhibited poor interfacial properties, namely significantly higher γ_{CMC}. This emphasizes the importance of having a FC tail in hybrid surfactants for generating appropriate interfacial properties for air/water and CO_2/water interfaces.

To examine the solubility and microemulsion stabilization by surfactants in $scCO_2$, the pressures at which a transparent single phases cloud, P_{trans}, were measured for water/surfactant/CO_2 mixtures at

various temperatures (35 – 75 ºC) and W_0 values. Figure 1 shows changes in P_{trans} as a function of temperature for each surfactant at W_0 = 0 and ~10. At values higher than P_{trans}, FC6-HC*m* (m = 4, 5, 6, 8) at [surfactant]/[CO_2] = 8×10^{-4} were soluble in scCO_2 with and without water. However, FC4-HC*m* (*n* = 2, 4) and HC6-HC6 always remained as a precipitate even at the highest pressure and temperature 400 bar and 75 ºC. FC6-HC2 was also insoluble without added water (W_0 = 0), but it became soluble for W_0 ≤ 4.

P_{trans} values at W_0 = 0 were comparable for the three FC6-HC*n* (*n* = 4, 5, and 6) surfactants but those for FC6-HC8 were higher than the others by 80-110 bar. At W_0 = 10, P_{trans} values of FC*m*-HC*n* elevated with HC length, *n,* in most cases, and were higher by >50 bar than those of the double FC-tail surfactant 4FG$(EO)_2$ reported earlier[13]. These significant increases in P_{trans} values with HC-tail length and number could be from increased attractive intermolecular interactions[4,14,21], promoting aggregation between reversed micelles. This effect of HC-tail causing high P_{trans} was found to be emphasized clearly upon addition of water. As P_{trans} became higher at lower temperature for FC6-HC*n*, the effect is likely to be accelerated due to the decreased temperature.[21]

Mid-range HC-tail lengths (*n* = 4, 5, 6) of FC6-HC*n* were observed to yield transparent phases with W_0 values up to at least 35, and the P_{trans} data obtained are shown in Figures SI3-SI6 (see supporting information). However, at W_0 higher than the solubilizing power of each surfactant as examined in Sec 3.2, the mixtures did not turn into a single phase even at the highest pressure available, and the symbols for P_{trans} at each W_0 are not displayed.

3.2 Solubilizing power of W/CO_2 microemulsions

To determine the solubilizing power, W_0^{max} (i.e. maximal W_0 solubilized by surfactant) 3 mmol L^{-1} aqueous methyl orange (MO) solution was loaded as a dispersed phase into the transparent single-phase CO_2 solutions with FC6-HC*n* (*n* = 4, 5, 6, and 8), and then UV-vis adsorption spectra were measured with increasing W_0. Alone, MO does not dissolve in pure CO_2 but it does dissolve in water, and is generally incorporated within the water-rich pockets of a single-phase W/CO_2 μE, dyeing the systems

red.[13,14] All transparent single–phases composed of surfactants and CO_2 were initially colorless, but turned reddish after loading the MO solution. The color became deeper with an addition of the MO solution, reflecting the reversed micelles encapsulating the loaded MO solution.

With addition of aqueous MO solution to surfactant/CO_2 mixtures, clear absorption spectra were obtained at different W_0 (see Figure SI7 in supporting information). A large and broad absorption peak of MO solubilized in the microemulsions was found at 360~520 nm. As the absorbance maximum λ_{max} shift to longer wavelengths[8,13,14] when MO molecules are solubilized in the more polar environment, λ_{max} can be employed as a probe of microenvironment polarity. The λ_{max} values for each hybrid surfactant were 410-430 nm and were close to those observed for double FC-tail surfactants (nFG(EO)$_2$ and nFS(EO)$_2$)[13], and therefore the reversed micellar polar microenvironments are expected to be similar. This implies that the surfactant tail structure did not affect aqueous core polarity, although the nature of the hydrophilic group, temperature and W_0 were found to affect polarity in previous studies using the double FC-tail surfactants[8,13,14].

From the spectra, changes in the absorbance at λ_{max} were plotted as a function of W_0, as shown in Fig. 2. Linear functions were obtained until certain W_0 values for each surfactant. The linear relationship and the appearance of the transparent single-phases demonstrates that the W/CO_2 μEs disperse increasing amounts of MO with increasing W_0. The point at which the linear relationship was broken was identified as the solubilizing power W_0^{max}. At higher than W_0^{max} the absorbance gradually decreased with increasing W_0, consistent with phase separation (e.g. Winsor-II W/CO_2 μE or liquid crystal-like surfactant precipitates) [13,14,29] occurring. The Winsor-II W/CO_2 μE (i.e. a W/CO_2 μE having separated excess water) and W/CO_2-type liquid crystal were indeed found over W_0^{max} for the double FC-tail surfactants by using high-pressure SANS.[29]

The solubilizing powers W_0^{max} have been extracted from Figure 2 and are clearly presented in Figure 3. As mentioned above, the hydrocarbon FC6-HC6 analogue HC6-HC6 and FC4-HCn (n=2 and 4) always gave two-phases of W/CO_2 mixtures, and were suggested to have no solubilizing power, namely $W_0^{max} = 0$. In comparison, for FC6-HCn, even for n-numbers of (n= 4, 6, 8), W_0^{max} decreased from 80 to

20 with increasing HC-tail length at 45 ºC, but it became almost constant (W_0^{max} = 50-60) with increasing temperature up to 75 ºC. Linear HC surfactant tails have been known to induce the attractive interactions between reversed micelles and destabilize W/CO_2 microemulsions (i.e. a poor W_0^{max} and/or a high P_{trans})[4,14,21]. However, the comparison in W_0^{max} values of FC6-HC*n* (*n*= 4, 6, 8) suggested the undesirable interactions of HC-tails are less prominent at higher temperatures due to increased thermal motion.

On the other hand, the shortest HC-tail hybrid surfactant FC6-HC2 exhibited poor solubilizing power W_0^{max} = 4. This probably resulted from the short chain ethyl group, which is an ineffective tail and hence gives a large critical packing parameter[19] and a low hydrophilic/lipophilic balance[18].

In the case of FC6-HC5, the W_0^{max} values at both temperatures were lower by 20-45 than those of FC6-HC4 and FC6-HC6. Due to small structural differences of just one methylene unit, the hydrophilic/lipophilic (or hydrophilic/CO_2-philic) balance of FC6-HC5 should be similar to those of *n* = 4 and 6. These data therefore display an odd-even effect[36] of surfactant HC-tails on W_0^{max}, offering a possible reason why the pentyl tail decreased W_0^{max} compared with the butyl and hexyl tails. From this stand point, even *n*-numbered HC-tails are suggested to be more suitable as hybrid surfactants for W/CO_2 microemulsions.

Most importantly, FC6-HC4 was found to have the highest solubilizing power of W_0^{max} = 80, a performance that is almost equal to the double FC-tail surfactant 4FG(EO)$_2$.[13] Here, to evaluate the effectiveness of fluorocarbon on W_0^{max} enhancement, W_0^{max}/N_F (where N_F is number of fluorines in molecule) values were compared for each surfactant. Those were 6.2 for FC6-HC4 and 4.4 for 4FG(EO)$_2$ [13], and the effectiveness per F-atom for FC6-HC4 was 1.5 times larger than that of 4FG(EO)$_2$. This implies that if a hybrid tail structure can be optimized it could boost the efficiency compared with a symmetrical tail structure of typical fluorocarbon surfactants used previously.

3.3 Effect of hybrid-tail structure of FC6-HC*n* on formation of W/CO_2 microemulsions

To examine the effect of the hybrid-tail structure on the shape and size of aggregates in FC*m*-HC*n* /D_2O/CO_2 mixtures, SANS *I*(*Q*) profiles were measured at W_0 = 20, 45 ºC and 350 bar. SANS data along

with the fitted $I(Q)$ functions are shown in **Figure 4**. SANS profiles are useful in determining the shape of nano- and colloidal particles. Under these conditions, HC6-HC6, FC4-HC2 and FC4-HC4 remained as a precipitate, and therefore no clear SANS profiles were obtained. On the other hand, FC6-HC*n* with n = 4-6 exhibited transparent single-phases giving clear SANS profiles. In the case of FC6-HC8, although a turbid phase appeared as W_0 reached the solubilizing power (W_0^{max} = 20), a SANS curve from D_2O droplets was observed.

In the low Q region (typically in the case of droplet microemulsions < 0.01 $Å^{-1}$), the scattering may scale as $I(Q) \sim Q^{-D}$, where D is a characteristic "fractal dimension" for the colloids; hence, the gradient of a log-log plot will be $-D$. In the case of non-interacting spheres, D should be zero in this low Q region, whereas D = 1 for cylinders and 2 for disks.[29,33] The FC6-HC*n* SANS profiles show D = ~0 for n = 4 and 8 and D = ~1 for n = 5 and 6, suggesting the presence of globular, and then rod-like nanodomains, respectively. One method to approximate radii and cylinder length from SANS data for the globular and rod-like microemulsions is via Guinier plots[29,33] (Ln [$I(Q)$] vs Q^2 for spheres and Ln [$I(Q)$ Q] vs Q^2 for cylinders) as shown in supporting information (**Figure SI7**). In the all plots of Ln [$I(Q)$] vs Q^2, linearity was obtained, and the gradients allowed estimation of radii of gyration, R_g (the slope = $-R_g^2/3$). This R_g may also be related to a principal sphere radius $R_{g\text{-sph}}$ as $R_g = (3/5)^{0.5} R_{g\text{-sph}}$ and cylinder length $L_{g\text{-cyl}}$ as $R_g = L_{g\text{-cyl}}/(12)^{0.5}$.[29,33] In other cases the Ln [$I(Q)$ Q] and Q^2 plots also exhibited linearity, and gradients were used to estimate cylinder radii, $R_{gui\text{-cyl}}$ (the slope = $R_{gui\text{-cyl}}^2$ / 4). The values $R_{g\text{-sph}}$ were calculated for the spherical microemulsions of FC6-HC4 and FC6-HC8, and $L_{g\text{-cyl}}$ and $R_{g\text{-cyl}}$ were calculated for FC6-HC5 and FC6-HC6: these values are listed in Table 2 along with R_g values.

The values of $R_{g\text{-sph}}$, $R_{g\text{-cyl}}$, and $L_{g\text{-cyl}}$ were employed as the starting points for model fit analyses using the full polydisperse Schultz ellipsoid and cylinder models. The parameter outputs are the average values of radii for the ellipsoidal D_2O cores ($R_{f\text{-ell,a}}$ and $R_{f\text{-ell,b}}$) and radius and length of the cylindrical one ($R_{f\text{-cyl}}$ and $L_{f\text{-cyl}}$). The polydispersity width was set at 0.3, which was assumed to be typical value for W/CO_2 microemulsion systems (e.g. 0.17-0.40 for double FC-tail sulfonate surfactants)[29]. These fitted parameters are also listed in **Table 2**.

For FC6-HC*n* reversed micelles, a very unique change in the D_2O core morphology was observed as a function of HC-tail length. Cylindrical core morphology was obtained for middle HC-tail lengths of n = 5 and 6, close to the FC-tail length (m = 6), with transitions into spherical nanodroplets occurring as the HC-tail became either shorter (n = 4) or longer (n = 8). The aspect ratios of the D_2O cores were calculated as 1.39 for n = 4, 5.45 for n = 5, 6.32 for n = 6, and 1.09 for n = 8. These results suggest an optimal FC/HC balance to stabilize cylindrical reversed micelles in $scCO_2$ where m/n = 6/6 (i.e. same FC and HC lengths). Why does this specific FC-HC balance drive the elongation of reversed micelles? From the standpoint that in the earlier reports most cylindrical reversed micelles in CO_2 have been obtained using hybrid surfactants, and only rarely with other types of surfactants. A key to resolving the question may be in characteristics special to hybrid surfactant, for example, FC- HC micro-segregation of self-assembled hybrid surfactant molecules.

To investigate aggregation properties of FC6-HC*n* (n = 4, 5, 6) in $scCO_2$, the aggregation number of surfactant per reversed micelle (N_{agg}) and occupied area per surfactant molecule at the W/CO_2 microemulsion surface ($A_{C/W}$) were calculated by following equations.

$$N_{agg} = C_{surf}/C_{micelle} \qquad (2)$$

$$C_{micelle} = (V_{D2O}\, C_{D2O} + V_{head}\, C_{surf})/(V_{core}) = C_{surf}\, (V_{D2O}\, W_0 + v_{head}\, N_A)/(v_{core}\, N_A) \qquad (3)$$

$$A_{C/W} = s_{core}/N_{agg} \qquad (4)$$

where N_A is Avogadro's number, C_{surf} and C_{D2O}, $C_{micelle}$ are molar concentrations of surfactant, D_2O and reversed micelle, V_{D2O}, V_{head}, and V_{core} are molar volumes of D_2O, surfactant headgroup and D_2O core, v_{core} and v_{head} are volumes per D_2O core ($V_{core} = v_{core}\, N_A$) and headgroup (e.g. v_{head} = ~215 $Å^3$ for sulfonate group, $V_{head} = v_{head}\, N_A$)[29], respectively. For $A_{C/W}$ calculation, s_{core} is surface area per D_2O core, and calculated from the shape parameters ($R_{f\text{-}ell,a}$, $R_{f\text{-}ell,b}$, $R_{f\text{-}cyl}$, and $L_{f\text{-}cyl}$) as well as the calculation of v_{core} for $C_{micelle}$.

According to critical packing parameter (CPP) theory[19], CPP can be also obtained by

$$CPP = v_{tail}/(A_{C/W}\, l_{tail}) \qquad (5)$$

where v_{tail} and l_{tail} are hydrophobic tail volume and length, respectively. According to this approach reversed micelles would be formed for surfactants with CPP > 1 (reversed cones form if the double-tail orients upward) to ~1 (cylindrical). If the hydrophobic part is assumed to be a truncated core, the volume should be[29]

$$v_{tail} = l_{tail}\{A_{C/W} + A_{tail} + (A_{C/W}\, A_{tail})^{0.5}\}/3 \qquad (6)$$

where A_{tail} is area per hydrophobic tail terminus, respectively. Then eq.(5) can be simply expressed as

$$\mathrm{CPP} = \{s_{micelle} + s_{core} + (s_{micelle}\, s_{core})^{0.5}\}/(3s_{core}) \qquad (7)$$

where $s_{micelle}$ is surface area per reversed micelle. In this study, the values of $s_{micelle}$ were calculated from the shape parameters ($R_{f\text{-}ell,a}$, $R_{f\text{-}ell,b}$, $R_{f\text{-}cyl}$, and $L_{f\text{-}cyl}$) and surfactant tail length l_{tail} assumed to be 13.4 Å (the length between the terminal F-atom and the C-atom bearing the sulfonate group). The calculated aggregation properties N_{agg}, $A_{C/W}$, and CPP are listed in Table 2. Another way to estimate $A_{C/W}$ is by using the Porod approximation to analyze SANS data[29]. However, unfortunately, for these weakly scattering systems, sufficiently accurate $\mathrm{I}(Q)\, Q^4\}_{Q\to\infty}$ values could not be obtained due to background noise.

A previous study reported that double FC-tail surfactants with sulfonate headgroups have $A_{C/W}$ = 117-129 Å^2, which were slightly larger than $A_{A/W}$ ($A_{A/W}$ = 94-118 Å^2)[13,29]. The larger $A_{C/W}$ values were suggested to occur due to CO_2-solvation into the surfactant tails as reported in the earlier papers[13,29], and this trend of $A_{C/W}$ being larger than $A_{A/W}$ was also observed in this study of hybrid surfactants. One large difference in $A_{C/W}$ for hybrid surfactants and double-tail surfactants is that $A_{C/W}$ values of FC6-HC*n* gradually increased from 101 to 149 Å^2 with increasing *n* from 4 to 6, in contrast with those of double-tail surfactants which were independent of tail length[29]. The differing effects of tail length on $A_{C/W}$ between hybrid and double FC-tail surfactants suggests intramolecular FC-HC repulsion to be more active in $scCO_2$, causing hybridized tails to be bulkier with a longer HC-tail. If so, intermolecular FC-HC micro-segregation would be also accelerated in $scCO_2$ compared with in atmospheric conditions. The elongated reversed micelles might result from the intramolecular repulsion and/or the intermolecular micro-segregation promoted with longer HC-tails (*n* = 5 and 6).

Earlier papers[29] found N_{agg} and CPP values at W_0 = 20 to be ~30 and ~1.5 for the double perfluorobutyl-tail surfactants in W/CO_2 microemulsions, respectively. In comparison, hybrid surfactants FC6-HC*n* have larger values of N_{agg} (=78-130) and CPP (> 1.6). The larger N_{agg} values were considered to be due to stronger intermolecular interactions such as π-π interactions and/or molecular shape[37] allowing the easy packing into large non-spherical aggregates. The larger CPP would act as an advantage to stabilize reversed micelle geometrically, and can be caused by larger $A_{C/W}$, as mentioned above.

4. Conclusions

W/CO_2 microemulsions are promising universal green-solvents for applications such as extraction, dyeing, dry cleaning, metal-plating, and organic or nanomaterial synthesis. These microemulsions should ideally be prepared with low levels of surfactant, be inexpensive and environmentally-benign. Therefore, finding a low F-content surfactant which generates a high solubilizing power is key to designing useful CO_2-philic surfactants.

This study examined the optimal tail structure for stabilizing microemulsions in hybrid FC*m*-HC*n* surfactants, and elucidated the causes of important findings seen previously [1]-[3]. As the results of phase behavior observations and absorbance measurements previously indicated, [1] optimal HC-tail length in the hybrid surfactant was found to be $n = 4$ at the shortest FC-tail length able to yield microemulsions ($m = 6$). The identification of an optimal HC-length is very interesting, since straight-chain HCs were commonly considered not to be CO_2-philic[3-5] and their inclusion in FC-surfactant molecules was limited in order to retain CO_2-philicity [2]. However, the maximum solubilizing power of FC6-HC4 was $W_0^{max} = 80$, a value equal to the highest performance yet reported in W/CO_2 systems[3-5,13-17,21,29]. To evaluate the effectiveness of each F-atom in the solubilization, the solubilizing power was divided by number of F-atoms in the molecule, and calculated as 6.2. This is 1.5 times larger than the most effective FC-surfactant in earlier papers[13]. The highest effectiveness per F-atom generated by hybrid structures is also an interesting concept for developing design theory of new CO_2-philic surfactants.

HP-SANS measurements characterized the D_2O cores of the FC6-HC*n* reversed micelles at $W_0 = 20$, and demonstrated [3] shape transitions in core morphology upon increasing HC-tail length (i.e. ellipsoid for $n = 4 \rightarrow$ cylinder for $n = 5$ and $6 \rightarrow$ sphere for $n = 8$). The aspect ratio was seen to reach 6.3 as a maximum at HC-tail length $n = 6$. Earlier papers[16,17] demonstrated the formation of reversed cylindrical micelles of hybrid surfactants; however, the role of the HC-tails in micelle elongation was unclear. Finding the optimal HC-tail length for the elongated reversed micelle could be a key to open this black box, and it implies the driving force belongs to intermolecular FC-HC micro-segregation.

A high water content W/CO_2 microemulsions, and the formation of elongated reversed micelles, could offer a new generation of universal solvents with unique properties. This is especially true if the elongated reversed micelles can increase CO_2 viscosity, which would significantly improve the poor efficiency of EOR CO_2-flooding[17]. Further W/CO_2 microemulsion studies on FC6-HC*n* will be focused on how reversed micelle morphology changes with concentration, W_0, and/or the other additives (metal ions, cosurfactants or hydrotropes)[38-40] and explore the use of elongated reversed micelle generation for increasing CO_2 viscosity for efficient EOR technologies.

5. ASSOCIATED CONTENT

Supporting Information. Surfactant synthesis for two hybrid surfactants (FC6-HC4 and FC6-HC5) and characterization by ^{1}H-NMR, FT-IR, and elemental analysis. Surface tension vs log (surfactant concentration) curves for aqueous surfactant (FC6-HC5 and HC6-HC6) solutions at 35 ºC. Change in P_{trans} as a function of temperature for W/CO_2 mixtures with FC6-HC*n* (*n* = 4, 5, 6 and 8) at [surfactant]/[CO_2] = 8×10^{-4}. UV-vis absorption spectra for FC6-HC*n* (*n* = 4, 5, 6 and 8)/CO_2 mixtures with 0.1wt% methyl orange aqueous solution at different W_0 values. Guinier plots (Ln [$I(Q)$] vs Q^2 and Ln [$I(Q)$ Q] vs Q^2) for D_2O/FC6-HC*n*/CO_2 mixtures at W_0 = 20, 350 bar and 45 ºC. This material is available free of charge via the Internet at "http://pubs.acs.org."

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Notes. The authors declare no competing financial interest.

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Figure captions

Figure 1. Changes in P_{trans} for surfactant/W/CO_2 mixtures with W_0 = 0 and 10 as a function of temperature. The molar ratio of the surfactant to CO_2 was fixed at 8×10^{-4}.

Figure 2. Absorbance maximum, λ_{max}, of MO in surfactant/W/CO_2 mixtures for different W_0 values at 350 bar. The MO concentration in water was 3 mmol L^{-1}. Molar ratio of surfactant-to-CO_2 was fixed at 8×10^{-4}.

Figure 3. Solubilizing power W_0^{max} of surfactants in scCO_2 at 350 bar and 45 or 75 ºC.

Figure 4. SANS profiles for surfactant/D_2O/CO_2 mixtures with W_0 = 20 at 45 ºC and 350 bar (CO_2 density = 0.92 g/cm^3). Fitted curves were based on a model incorporating a Schultz distribution of polydisperse ellipsoid or cylinder particles. The molar ratio of the surfactant to CO_2 was fixed at 8×10^{-4}.

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